

DYNAMIC BEHAVIOUR OF MIXER-SETTLERS

GHARIB S ALY

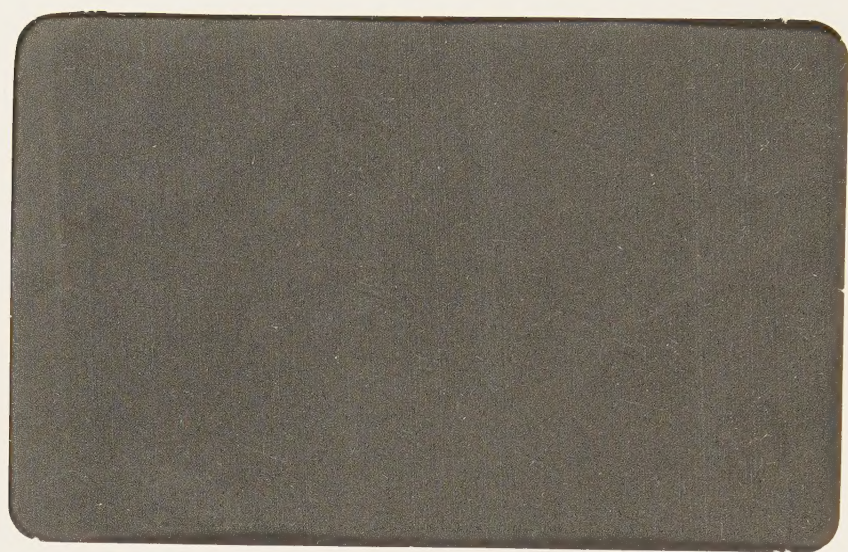


**DEPARTMENT
OF
CHEMICAL ENGINEERING**



AVDELNINGEN FÖR KEMISK APPARATTEKNIK

**LUND INSTITUTE OF TECHNOLOGY
LUND – SWEDEN**



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Gharib S Aly, Department of Chemical Engineering,
Lund Institute of Technology, Lund, Sweden

This thesis consists of this summary and of the following papers:

- I. Aly, G.; Jernqvist, A.; Reinhardt, H.; Ottertun, H.
Dynamic Behaviour of Mixer-Settlers
Part I: A New Experimental Technique
Chem. Ind. 1971, 57, 1046-1048.
- II. Aly, G.; Wittenmark, B.
Dynamic Behaviour of Mixer-Settlers
Part II: Mathematical Models and Identification Methods
J. appl. Chem. Biotechnol. 1972, 22, 1165-1184.
- III. Aly, G.; Ottertun, H.
Dynamic Behaviour of Mixer-Settlers
Part III: Testing Mathematical Models Using Flow Rates as Input Signals
J. appl. Chem. Biotechnol. 1973, 23, 643-660.
- IV. Aly, G.
Dynamic Behaviour of Mixer-Settlers
Part IV: The Cadman-Hsu Model
Proceedings, International Solvent Extraction Conference (ISEC 74),
1974, 1, 189-229.

INTRODUCTION

Solvent extraction equipment can be divided into stagewise contactors and differential contactors. The first group includes mixer-settlers, rotating disc contactors, multiple-mixer columns, etc; the second includes packed, spray and, under certain conditions of operation, pulsed columns.

A mixer-settler is a device for bringing about equilibration and subsequent separation of two immiscible liquid phases. A number of such stages can be arranged in series to give counter-current operation.

This type of contactor has been in industrial use since about 1904. The earliest countercurrent mixer-settler appears to be that of Barstow¹, in which the flow pattern of the two phases is cocurrent through each mixing and settling stage but countercurrent over-all. Mixer-settlers are essentially simple in design, have a high efficiency, high flexibility, large residence time, low hydrostatic head and are relatively easy to scale up and control. A main disadvantage, especially in the extractive metallurgical industry, is that at any given time, the bulk of the solvent is in the settlers and the solvent-inventory cost becomes an appreciable fraction of the capital cost of the extraction process.

While mass transfer operations are of great industrial importance, the dynamic characteristics of diffusional processes have received little attention, mainly because of incomplete understanding of the mechanism of mass transfer by molecular and eddy diffusion, and partly also because of the difficulty of correlating steady-state results. Since the pioneer work of Marshall and Pigford², the process dynamics of solvent extraction has received much attention. Unfortunately, experimental work has lagged because of the difficulties involved in obtaining accurate response measurements. A number of problems not encountered in steady-state analyses are found when dynamic measurements are attempted.

The present thesis is concerned with the dynamic behaviour of extraction processes. This is important for several reasons:

1. A knowledge of the dynamic behaviour of a process is necessary for the design of control systems. The dynamic response of a process and of the controllers involved must be known if the control of the process is to be successful. In order to assess the controlled performance of a process and to allow different control strategies to be computed at the design

stage, information is required on the transient response of the variables controlled to different disturbances and load changes.

2. Design calculations for most chemical engineering systems have hitherto been based on steady-state behaviour. Dynamic information gives a better understanding of process phenomena. This can lead to more reliable design methods and there is no doubt that, for instance, scale-up procedures using dynamic parameters will become significant in the future.
3. While it may be desirable for a process to run under steady-state operation conditions, there will be inevitable upsets, shutdowns and startups. For example, the distribution of solutes is governed by some form of the distribution law but mechanical or design imperfections in the process may not allow the correct value of the distribution coefficient to be obtained. This will cause some recycle of solutes in the system and hence the outputs of the extractor will not be constant. Furthermore, in an extractor operating under conditions of perfect hydrodynamic equilibrium, any volume input transient is instantly transmitted throughout the unit to the end remote from the transient input. Solute mass will be transferred with the volume transient causing an upset in the mass equilibrium in the system. Dynamic information enables a plant engineer to predict the rate at which a piece of equipment proceeds to equilibrium from a given initial state. A knowledge of the equipment dynamics can also measurably reduce the time required to shift the operating conditions from one level to another which may be more efficient.
4. The dynamic approach can be used to test postulated mathematical models, and to obtain a quantitative validation for the underlying assumptions.
5. The dynamic approach can also be applied to full-scale plants in order to identify disturbances and to indicate the changes that should be made in the system to yield the desired response. It implies of course adaptive and computer control.

Having decided that a knowledge of the dynamic response is important, one seeks a method for determining this information. In practice, some type of input perturbation is used to excite the dynamic characteristics of the piece of equipment under consideration in order to produce a change in one or more of the output variables. This input disturbance may be in the form of step changes, pulse changes, sinusoidal signals or pseudo random binary sequences (PRBS).

A comprehensive survey of the literature on the dynamic behaviour of solvent extraction processes was presented in 1969 by Pollock and Johnson³. Their review shows that in the area of transient and frequency response analysis, the greatest attention has been paid to pulsed, packed and Schiebel type columns. However, during the last few years, some valuable papers have been published dealing with the dynamics and control of other types of extraction contactors. Apelblat and Faraggi⁴ have investigated theoretically a linked extraction-stripping system and constructed an analogue model consisting of a network of variable resistors and capacitors having the equivalent of 15 stages. The input to the system was a square wave, and the response at various stages was measured on an oscilloscope. Their model was corrected for Murphree stage efficiency and for the effective rather than the geometrical stage hold-up. Solute equilibria were included in the model but they did not study any specific extraction system. Jones and Wilkinson^{5,6,7} have obtained solutions for the transient response of a stagewise extraction column with linear equilibrium, by solving numerically the Laplace-transformed differential stage relationships. The accuracy of their model is limited to some extent by the simplifying assumptions made, in particular the linear equilibrium relationship and the constancy of the backmixing parameters, holdups and mass transfer coefficients throughout the column. Nevertheless, this model should be of value in control studies of stage-wise contactors. Ingham and Dunn^{8,9} solved the model of Jones and Wilkinson using the MIMIC digital simulation programme, which is based on a Runge-Kutta-Merson routine. They presented solutions for a 5 stage and a 23 stage column and produced results which are claimed to be in good agreement with those of Jones and Wilkinson. However, no experiments were carried out to test the validity of the theoretical work presented. McDonald and Wilkinson¹⁰ have recently presented a control study of a multiple-mixer column. Their results show that feedback control is not satisfactory and a control system involving feedforward control was proposed as a more suitable arrangement. Almost the same conclusion was reached by Cadman and Hsu¹¹ in studies of theoretically controlled extraction systems using steady-state feedforward, three-mode feedback and a combination of these. Their work has been treated separately in Part IV of this thesis.

SUMMARY OF THE PRESENT WORK

PART I

Difficulties in obtaining accurate dynamic response measurements which are not encountered in steady state analyses have held back experimental work in the field of extraction dynamics. Burns and Hanson¹² in experimental studies of the dynamic response of a five-stage mixer-settler unit applied the tedious "stop-start" procedure in order to overcome the volumetric transient caused by the removal of samples. They were able to achieve only discrete measurements of the aqueous phase concentration.

In Part I, the applicability and suitability of the AKUFVE¹³ measuring technique, based on the use of radioactive tracers, was tested. The AKUFVE, developed at the Department of Nuclear Chemistry, Chalmers University of Technology, consists of a mixing chamber, a centrifuge and a recycle system. It thus permits continuous mixing, phase separation and recycle. Advantage may be taken of the recycle loops to install on-stream analytical devices which will continuously record metal ion concentrations. Provision is also made for addition of reagents such as acid, alkali and extractant directly to the mixer in order to vary the extraction conditions. The equilibrium relationships for the Alamine 336 and the LIX 64N systems were determined by the AKUFVE. Only the centrifuge part of the AKUFVE has been used in the dynamic studies here.

This technique enables the concentration of each phase to be continuously and accurately analysed on-line without imposing any volumetric transient on the equipment. A total time delay of 5 seconds was attained for analysis of the contents of the mixer part of a stage. In analysing the settler response, two small pumps were used instead of the centrifuge.

Amine extraction of copper was chosen as a suitable chemical system for the present studies due to its industrial significance. ⁶⁴Cu was used as the radioactive tracer because of its relatively short half-life. A calibration procedure for the active copper solutions was developed to guarantee constant specific activities in all of the copper solutions used during the experiments.

A 4-stage mixer-settler pilot plant was constructed and used to test this measurement technique. A modified version of the conventional pump-mix type of mixer-settler was chosen in which the lifting device for the aqueous phase and the mixing device for both phases are connected on the same shaft, as seen in Fig.1.

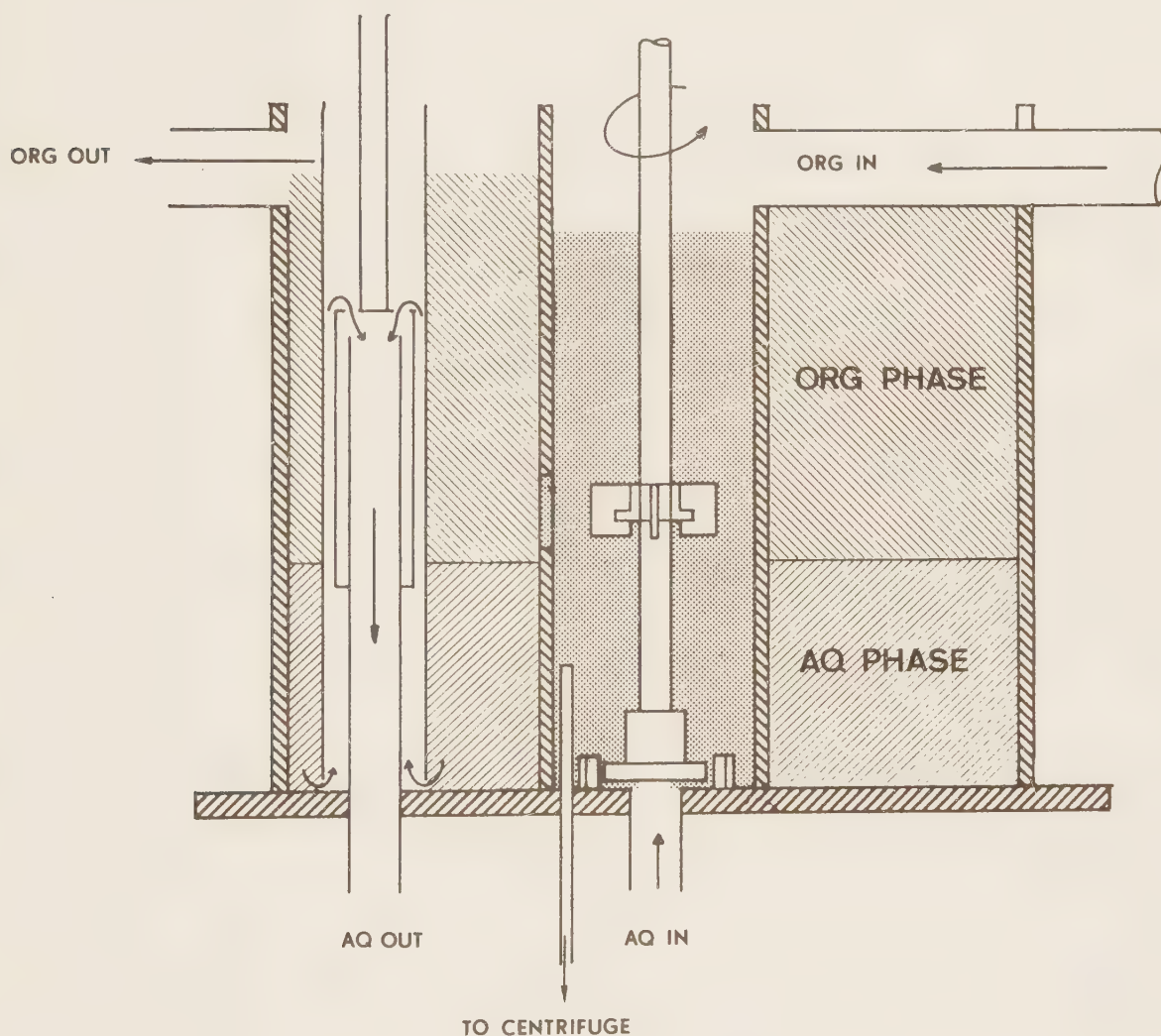


FIGURE 1. A SCHEMATIC MIXER-SETTLER STAGE

Scintillation detectors together with a data acquisition and recording system were incorporated to measure and record the experimental responses directly on paper tape.

This experimental technique enabled the collection of large amount of response data describing the dynamic behaviour of the mixer-settler unit. Step and PRBS input signals were applied in the four control variables, i.e. the inlet concentrations and flow rates.

PARTS II-III

Almost all theoretical and numerical work published in the field of extraction dynamics has been built on one of the four basic models:

1. two phase stagewise contact with ideal mixing in each stage,
2. two phase stagewise contact with backmixing,
3. two phase differential contact with plug flow, or
4. two phase differential contact with axial mixing.

As far as mixer-settlers are concerned, the mixer unit is always assumed to be a perfectly mixed equilibrium stage with constant phase holdups. This is due to the fact that detailed mixing information specifying additional factors such as short-circuiting and dead zones will generally not be available. For the settler, two extreme cases may be noted, namely, perfect mixing within each phase on one hand or plug flow from inlet to exit on the other hand. Intermediate cases may be visualised as a combination of short-circuiting flows and segregated regions in which perfect mixing is approximated. Some authors assume the organic phase to move in plug flow while the aqueous phase is perfectly mixed¹⁴.

Two mathematical models are considered in Part II. Both models assume ideal mixing in each stage, a linear equilibrium relationship, constant flow rates and immiscible liquid phases. The first model assumes constant phase holdup throughout the mixer-settler unit and equilibrium conditions. The Murphree stage efficiency for the organic phase was introduced in the second model where it was also assumed that phase holdup is independent of time and varies only with the stage number. These simple equilibrium models give a fairly good simulation of the process, especially when the extraction system contains a considerable number of stages¹⁵. The experimental data used to test these models represents the response to different input signals using the inlet aqueous phase concentration as a control variable.

Transfer functions, describing input-output relationships between the various concentrations in the unit, were determined and analysed. The results obtained show that there are fast and slow time constants for an extraction system. The fast time constant is due to the immediate mass transfer of solute in the mixer, while the slow time constant is due to the recycle streams involved in the multistage system.

Experimental data allow the determination of some of the unknown parameters in the mathematical models. Suitable methods are described in the literature¹⁶ and these provide very useful tools for the derivation of mathematical models for the process industries, particularly in cases when model building from physical and chemical laws is difficult or gives models that are too complex. Schematically the different stages of identification are shown in Fig. 2 which indicate the most important relations¹⁷. Starting with available *a priori* knowledge of the process and the intended use of the model in mind, experiments can be designed and possible model structures suggested. The experimental data are then used for estimation and verification. The final result may be an acceptable model.

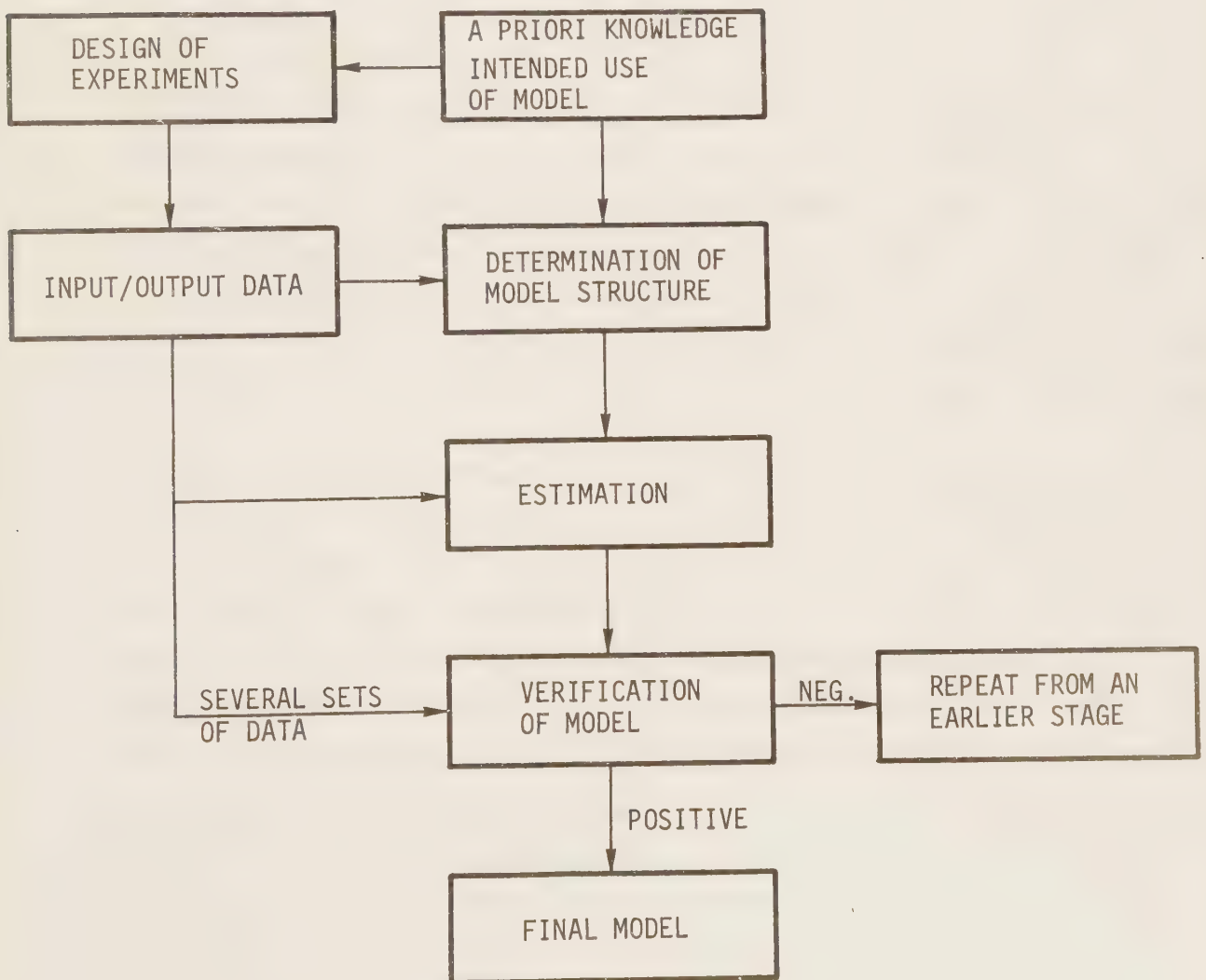


FIGURE 2. THE IDENTIFICATION PROBLEM SCHEMATICALLY SHOWN¹⁷

The two models described here were tested with experimental data, using two identification methods: the maximum likelihood method (ML-method) and identification of state space models. The ML-method gives only input-output models and does not use any physical knowledge of the process for the derivation of the model. The model obtained can be used to determine different controllers for the process. The second method is based on a state space model for which it is necessary to postulate the model structure from physical considerations. This means that the structure of the model is well defined but the model contains some unknown parameters, for instance mass transfer coefficients, phase holdups, backmixing parameters, etc. This method can thus be used to estimate these unknown physical parameters as well as to design controllers for the system. The ML-method showed that a mathematical model of the second order gives a good description of the dynamic behaviour of the extraction process considered here. Identification of state space models gives estimates of the values of some static parameters: the slope of the linear equilibrium relationship and the phase holdups. The estimated value of the slope agreed very well with the experimental value while the estimated values of the phase holdups were somewhat higher than expected. These higher values can be accounted for by the turbulent flow in about 7% of the settler part which can thus be considered as a continuation of the mixer part. It was found that both models are dynamically equivalent since the Murphree efficiency was used as a static property of the system.

In Part III, the two mathematical models are modified and generalised so that the four inlet parameters can be used as control variables. Aqueous and organic phase flow rates were used as input signals while the response consisted of the exit concentrations from the fourth stage of the mixer-settler unit. The computing programs, the sampling method and two numerical examples are outlined to illuminate the mathematical models and the method of identification of state space models.

It was concluded that linearised models are adequate for simulating the dynamic behaviour of such contactors. Furthermore, it was confirmed both experimentally and by the identification method that the ratio between the volumetric phase holdups in the mixer part is nearly equal to the ratio between the volumetric flow rates entering the mixer-settler unit.

PART IV

The dynamics and control of multi-stage mixer-settlers has recently been dealt with by Cadman and Hsu¹¹ in a substantial theoretical study. They derived non-linear dynamic models based on instantaneous overall and component mass balances and on non-linear equilibrium relationships. Three main assumptions were made, namely: perfect mixing, perfect stage efficiency and negligible density variation with composition. As far as the assumption of perfect mixing is concerned, plug settler flow would be more realistic and naturally, if additional mixing information is available, more sophisticated models can be used. Several different variations were formulated including constant and non-constant holdup volume in the mixer, constant total holdup volume in the settler with both variable and constant individual phase holdups. The bulk of their work involved the case with constant holdups only.

Three equations were written for the mixer giving the overall material balance and the two component material balances. The settler was described by seven equations using the same principle. Three non-linear equilibrium equations were used to describe the chemical system. We thus have 13 equations which completely define a mixer-settler stage. These include 13 unknown time variables; 10 concentrations and 3 flow rates. The question is how to solve them.

The non-linear model was linearised about steady-state operating conditions and on solution, using the Laplace transformation technique, Cadman and Hsu developed transfer functions for one mixer, one settler, a combined stage and finally a two-stage unit. The main thrust of the control portion of their study involved numerical investigation of a two-stage unit with a hypothetical ternary system. Hsu¹⁸ indicated how analytical transfer functions can be developed for higher order models but derivations become extremely complex and tedious and it would be easier to develop these transfer functions numerically from simulation rather than analytically. The algebra is laborious for the two-stage case and will of course get prohibitively complex for the multi-stage cases.

Since the work of Cadman and Hsu appears to be by far the most complete study of the control of stagewise extractors, it was decided to undertake a continuation of their work for future needs. Part IV of this thesis has three main objectives:

1. To derive a straightforward solution and construct a digital computer programme allowing for a more realistic number of stages (more than two),
2. To test the model experimentally,
3. To compare the model with the more simple one described in Part II.

The solution obtained using matrix notation and variable elimination gave results very similar to those published by Cadman and Hsu. For the experimental verification, the first experiment mentioned above in Part III was used. The model simulation yielded good agreement between theoretical and experimental responses with a relative error less than 2.5%.

The comparison between the Cadman-Hsu model and the simpler one showed that the simulated responses for both phases in both models were almost coincident. This shows that a relatively simple model can describe the dynamic behaviour of such contactors provided the number of stages encountered is greater than two. This is of considerable importance for computer memory capacity and for the simulation time required. Almost the same conclusion was drawn by Halligan and Smuts¹⁴ who simulated the approach to steady state of a single mixer-settler unit, a three stage unit and a six stage unit using an analogue simulator.

FUTURE PROSPECT

This thesis represents merely a stage in the development of concepts and techniques in the field of extraction dynamics. These techniques appear promising and it is to be hoped that they can be developed much further.

It is planned to do further research within the framework of the present investigation, especially in applications to full-scale industrial processes. To control such processes effectively, optimal control systems will be constructed and tested in co-operation with the Department of Automatic Control in Lund.

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